

## THERMOGRAVIMETRIC AND FREE RADICAL EVIDENCE FOR IMPROVED LIQUEFACTION OF COAL WITH WASTE TIRES.

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### ABSTRACT:

Thermogravimetry and in-situ electron spin resonance spectroscopy of free radicals are used to investigate the coprocessing of blind canyon coal with waste tire rubber (Goodyear Vector) and with polystyrene and polyethylene. Temperature-programmed thermogravimetry shows improved conversion and the data of free radical density versus temperature to 500°C, under vacuum and flowing H<sub>2</sub> gas conditions, show that waste tires act as good hydrogen donors. These findings suggest improved liquefaction of coal with waste rubber. Similar experiments of coprocessing of coal with polystyrene and polyethylene shows enhanced hydrocracking indicated by a large increase in the free radical densities above 350°C.

### INTRODUCTION:

The free radicals in coals as monitored by electron spin resonance (ESR) spectroscopy are an integral part of the coal structure since their characteristic properties vary systematically with coal rank and coal macerals [1,2]. As coals are subjected to pyrolysis, new free radicals are generated due to coal depolymerization whose intensities vary in a systematic fashion with pyrolysis temperature in bituminous coals [3-5]. In the process of direct coal liquefaction, hydrogenation of the products of coal pyrolysis must occur resulting in the capping of the free radicals by transferred hydrogen [6-8]. Therefore a decrease in the free radical density upon hydrogenation is indicative of the liquefaction process. Consequently ESR spectroscopy is an important experimental technique for coal conversion studies if the experiments can be carried out in-situ under the practical conditions of high temperatures and pressures used in coal liquefaction. Recently we have developed such an ESR apparatus in which in-situ experiments for temperatures up to 600°C can be carried out under various atmospheres such as vacuum, flowing gases and H<sub>2</sub> pressures up to 700 psi [9]. In the work reported here, we have employed this apparatus to investigate the coprocessing of coals with waste tires and we provide definite evidence of significant enhancement of coal hydrogenation facilitated by the tire polymers. These results are supportive of the increased coal liquefaction yield in the presence of waste tires reported first by Farcasiu and Smith [10] and more recently by Liu et al [11]. Similar experiments on the coprocessing of coal with polyethylene and polystyrene show a rapid increase in the free

$$N = \left( \frac{N_T T}{298} \right) \frac{m_c}{m_T M} \quad \text{----- (1)}$$

where  $N_T$  is the measured free radical density at any temperature  $T$  and  $(T/298)$  corrects for the Curie law variation of the free radical density relative to room temperature (298K),  $m_c$  is the mass of coal at room temperature,  $m_T$  is the mass of the mixture at any temperature, and  $M$  is the total mass at room temperature. For the ESR measurements in sealed configuration only the Curie law corrections are applied. From Figs. 3 and 4, for measurements in sealed and under hydrogen flow configurations, it is clearly evident that above  $\sim 400^\circ\text{C}$ , the tire polymer has considerable effect in reducing the coal free radical densities. The following points are noteworthy.

At the lower temperatures of around  $100^\circ\text{C}$ , there is a slight increase in  $N$  due to the effect of tire. Above  $400^\circ\text{C}$ , the  $N$  values in the presence of tire are suppressed by a factor of two to three and the presence of  $\text{H}_2$  appears to provide additional suppression of the free radical density. In Figs 5 and 6 the variation of free radical densities with temperature is shown for the coal mixed with polyethylene or polystyrene. Here, above  $350^\circ\text{C}$  there is very rapid increase of free radicals compared to the coal alone. Since a large mass loss occurs in this temperature, the mass corrected free radical densities show a very large effect. The free radical densities shown in Figs 5 and 6 include plots for both with and without the application of mass correction. In either case, we see enhanced hydrocracking in the coprocessing of coal with polymers and beyond  $450^\circ\text{C}$ , the increase in  $N$  is by a factor of 3 to 6. The importance of these results is discussed next.

In a recent paper Shin et al [12] have reviewed the effect of hydrogen on the free radicals and it is argued that in addition to the generally accepted view of the capping of the free radicals by hydrogen in the hydrogenation process, hydrogenolysis can also occur in the initial stages of the reaction (Hydrogenolysis should increase  $N$  whereas hydrogenation should lower  $N$ ). The results presented in Figs. 3 and 4 show an initial increase in  $N$  at lower temperatures due to the coal-tire interaction and this may be due to hydrogenolysis. The rapid decrease in the free radical density at the higher temperatures in Figs. 3 and 4, is most likely due to hydrogenation facilitated by the transfer of hydrogen from tire polymers to coal fragments. The liquefaction experiments of Farcasiu and Smith [10] carried out  $425^\circ\text{C}$  and those of Liu et al [11] at  $400^\circ\text{C}$  also indicate increased conversion of coal in coprocessing with waste tires. Our results also indicate that significant coal liquefaction occurs in the presence of tires and that the tires act as excellent hydrogen donors. The polyethylene and polystyrene mixed with coal, on the other hand, promote rapid hydrocracking of coal.

radical densities beyond  $\sim 350^{\circ}\text{C}$  indicating enhanced hydrocracking of coal with these polymers. These results are described below.

## EXPERIMENTAL RESULTS AND DISCUSSION

The ESR studies reported here were carried out on a Blind Canyon coal obtained from the Penn State Coal Bank. The analysis of this coal as well as details of the x-band high temperature ESR cavity system were given in a recent paper [9]. The tire polymer used in these experiments was chipped from a used tire (Goodyear Vector) and it was mixed with the coal in 1:1 ratio with mortar and pestle. Two samples of tire were cut from the central portion and from the rim of the tire and are referred to as tire(C) and tire(R) respectively. Polyethylene (spectrophotometric grade) and polystyrene (mol. wt.  $\sim 2500$ ) were obtained from Aldrich Chemical company Inc. Polymers were mixed 1:1 with coal for TG and ESR measurements. For ESR, experiments were carried out under vacuum conditions (sealed tube) and in flowing  $\text{H}_2$  gas at a flow rate of  $100\text{cc/m}$  [8,9]. We also measured the weight loss in thermogravimetry in flowing  $\text{H}_2$  gas ( $100\text{cc/m}$ ) at a heating rate of  $10^{\circ}\text{C/m}$  using a Mettler TA3000 system.

Fig. 1 shows the remaining weight (%) as a function of temperature for the Blind Canyon coal, the tire and the tire coal mixture in a flowing  $\text{H}_2$  experiment. Most of the weight loss due to release of volatiles occurs between  $300$  and  $500^{\circ}\text{C}$  and it is clearly evident that the coal-tire mixture has the highest weight loss. There is no significant difference between the samples cut from the central or rim part of the tire in the variation of remaining weight with temperature. If we use the weight loss due to volatiles as the percentage conversion, then at  $500^{\circ}\text{C}$ , the percentage conversions for coal, tire and coal-tire respectively are about 32%, 48% and 66%. The presence of tire polymers has clearly enhanced the percentage conversion of coal. Fig. 2. shows the plots of remaining weight (%) as a function of temperature for the polyethylene and polystyrene and for coal mixed with these polymers. For these cases also we see that the weight loss in the mixture is greater than a simple addition of weight loss of coal and polymer alone. Note also that in the mixture the major weight loss occurs at temperatures different from that for the individual polymers indicating strong reaction of polymers with coal.

For the ESR experiments, samples were either vacuum sealed in the ESR tube at room temperature followed by measurements at elevated temperatures or measurements were done in flowing  $\text{H}_2$  gas [8,9]. Only a single ESR line is observed from the coal sample and no ESR signal was observed from the tire or polymers as determined in a separate experiment up to  $500^{\circ}\text{C}$ . In Fig. 3 we show the temperature variation of the free radical density  $N$  for the coal and the coal-tire(R) mixture in sealed configuration and in Fig 4. for hydrogen flow configuration. For measurements in hydrogen flow the values of  $N$  plotted are determined by the equation(1):

In summary, the results presented here on the free radical density of coals during coprocessing with tire and polymers suggest that tire polymers lower the free radical densities and act as good hydrogen donors. On the other hand polyethylene and polystyrene promote rapid hydrocracking of coal. Both of these findings are positive indicators for improved liquefaction of coals coprocessed with waste tires and polymers.

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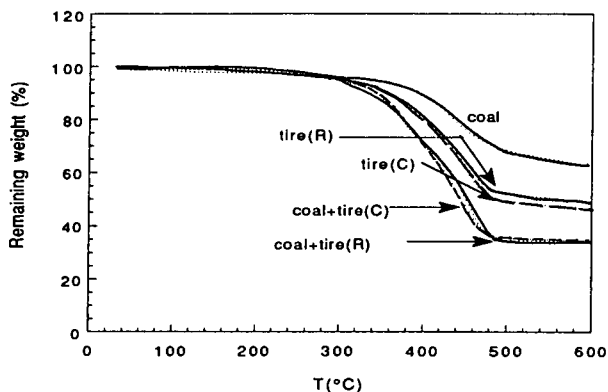


Fig 1. Remaining weight as a function of temperature for coal and coal tire mixtures (1:1 by weight). Tire(C) and tire(R) are cut from the central and rim portions of the tire. All measurements were done in flowing hydrogen.

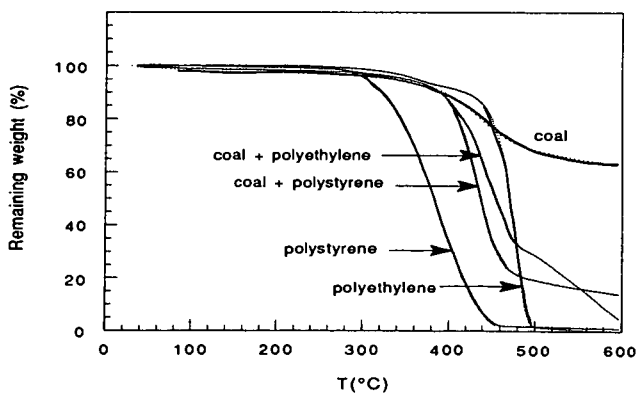


Fig.2. Remaining weight as a function of temperature for coal and coal mixed with polyethylene and polystyrene(1:1 by weight) Measurements were done under hydrogen flow.

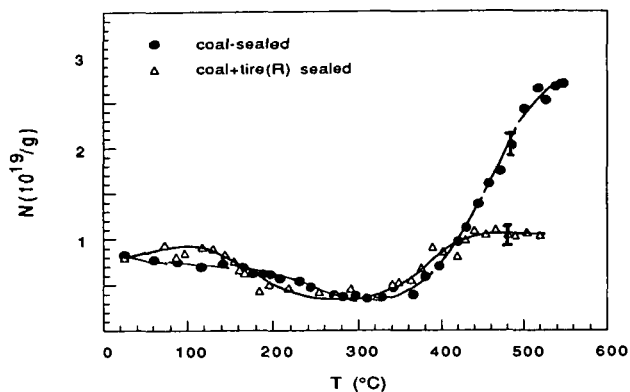


Fig 3. Variation of free radical densities with temperature for coal, and coal mixed with tire(R) (1:1 by weight). Samples were evacuated and sealed. No corrections for mass changes were applied.

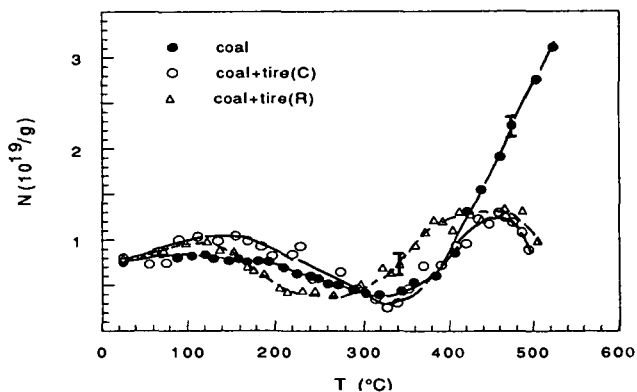


Fig. 4. Variation of free radical densities with temperature for coal and coal tire mixtures (1:1 by weight). Measurements were done under hydrogen flow. Free radical densities are corrected for changes in mass.

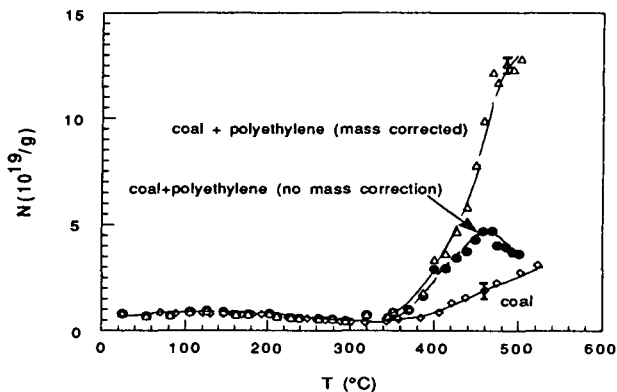


Fig 5. Variation of free radical densities for coal and coal mixed with polyethylene (1:1 by weight). For the mixture,  $N$  is plotted both with and without the mass correction.

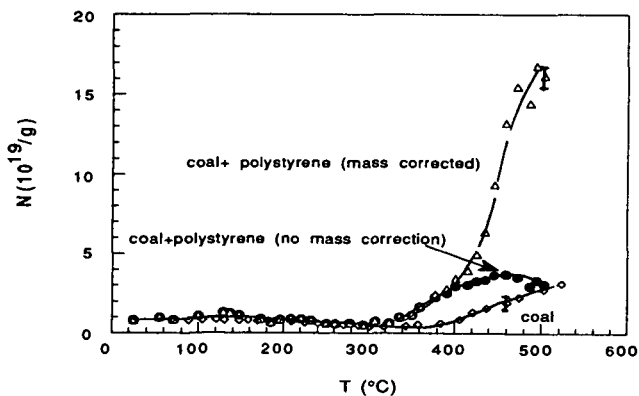


Fig 6. Variation of free radical densities for coal and coal mixed with polystyrene (1:1 by weight). For the mixture,  $N$  is plotted both with and without the mass correction.

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